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13. ABSTRACT (Maximum 200 words)

ROMP polymerization has become an important method for the preparation of polyphenylenevinylenes and polynaphthylenevinylene. The new route allows the band gap and processing properties of the polymers to be varied by the use of side chains and functional groups. These materials are being used to fabricate electroluminescent devices with tunable colors. New techniques have been developed for the synthesis of the starting barrelenes and benzobarrelenes. These synthesis start from the ICI diol system that was used in the preparation of polyparaphenylene. A key to these developments is the availability of well defined catalysts, considerable effort has been devoted to the design and synthesis of new complexes that will catalyze the ROMP polymerization reaction and to develop new procedures which will control the molecular weight and livingness of those systems know. The students involved in this work have gained experience in polymer synthesis, catalyst development and the fabrication of devices.

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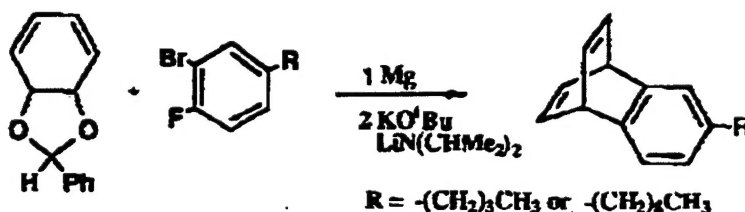
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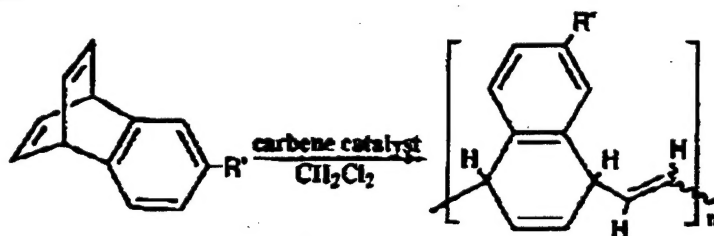
## Final Report Polyarylenevinylene

The ICI cyclohexadiene monomer has been used to prepare poly(arylenevinylene) derivatives through a precursor route. The polyarylene vinylenes show interesting properties and some derivatives have been used to fabricate photoemitting diodes.

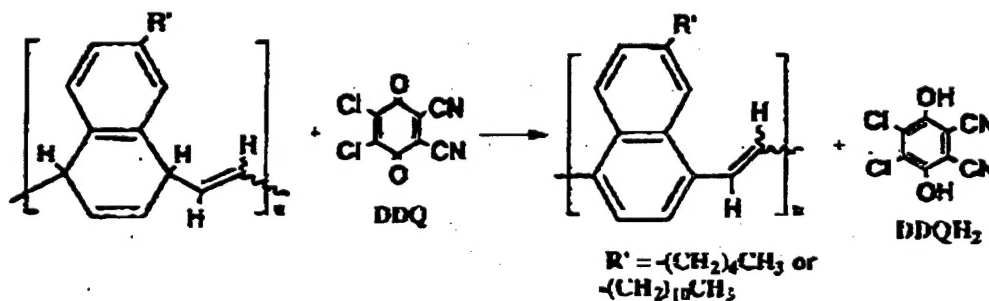
A general route to polynaphthalene vinylenes has been developed that is now being expanded in to the synthesis of block polymers. A simple route to substituted benzyne precursors was developed and the resulting benzyne were added to the ICI monomer. The adducts could be converted to benzobarrelene analogs by the treatment of the benzaldehyde acetal derivative with a strong base such as LDA.



The resulting benzobarrelenes could be polymerized to in high yields with a variety of ROMP catalysts. These living systems could be used to control the molecular weight and molecular weight distribution.



The resulting soluble polymers could then converted to the soluble vinylenenaphthylene with a variety of oxidizing agents, however DDQ was the most effective.

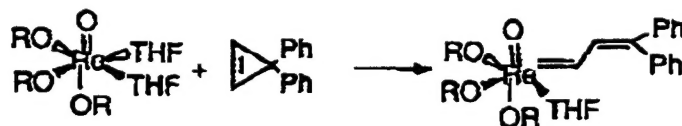


The UV/Vis spectrum of the fully conjugated derivatives displays a strong absorbance at 448- 450 nm, which demonstrates the formation of an extended p-conjugation in the oxidized polymer after the dehydrogenation. When excited at 440 nm, the fluorescence emission spectra of the conjugated polymers show strong signals at 583 nm and 572 nm respectively. By visual observation, solutions of the conjugated polymers glow yellow orange under UV irradiation. In preliminary studies, electroluminescence devices have been fabricated by spin coating using these materials. A key finding was that good internal electroluminescence quantum efficiencies of up to 0.05% could be obtained using an air stable Aluminum electrode.

Derivatives that contain halogens as electron withdrawing groups have been prepared and converted to polymers. It has been found that these derivatives can be used to tune the emission spectrum of the resulting polymer for example a polymer with red fluorescence has been reported. With support from another agency, this work has continued as a method for the preparation of a variety of block polymers and related systems. A number of new methods of controlling the polymerizations were uncovered during this work and the mechanism of control was studied in detail with support of the NSF.

### New ROMP Catalysts

Since ROMP polymerization has become an important method for the preparation of polyphenylenevinylene polymers, new catalysts that are tolerant of functional groups are required. Rhenium based heterogeneous catalysts have shown unusual stability in the past to functional groups.



Our group is involved in the development of well defined, soluble catalysts which was expected to show much better stability and selectivity. Although the complex was an active metathesis catalyst, it did not compete with early metal catalysts in terms of rate and late metal catalysts in terms of functional group tolerance. Further studies on this system were carried out at DuPont.

### Publications

"Synthesis, Structure and Reactivity of a Rhenium Oxo-Vinylalkylidene Complex." B. T. Platt, R. H. Grubbs, R. L. Blanski, J. C. Calabrese, and J. Feldman, *Organometallics* 1994, 13, 2728-2732.

"Synthesis of Poly-(1,4-Naphthalene Vinylene)s: Metathesis Polymerization of Benzobarrelenes." L. Pu, M. W. Wagaman, and R. H. Grubbs, *Macromolecules* 1996, 29, 1138-1143.

"Red-Orange Electroluminescence with New Soluble and Air-Stable Poly(Naphthalene-Vinylene)s." S. Tasch, W. Graupner, W. Leising, G. Pu, M. W. Wagaman, and R. H. Grubbs, *Advan. Mater.* 1995, 7(11), 903.

"Synthesis and Photoluminescence Properties of Polynaphthalenevinylene (PNV) Homopolymers and Block Copolymers Synthesized by Ring Opening Metathesis Polymerization (ROMP)." M. W. Wagaman, E. Bellmann, and R. H. Grubbs, *Philosophical Transactions of the Royal Society* 1997, 355, submitted.

"Synthesis of PNV Homo- and Copolymers by a ROMP Precursor Route." M. W. Wagaman and R. H. Grubbs, *Synthetic Metals*, submitted.

Directly Related Papers supported by parent grant:

"Routes to Conjugated Polymers with Ferrocenes in their Backbones: Synthesis and Characterization of Poly(ferrocenylene divinylene) and Poly(ferrocenylene butenylene)." C. E. Stanton, T. R. Lee, R. H. Grubbs, N. S. Lewis, J. K. Pudelski, M. R. Callstrom, M. S. Erickson, M. L. McLaughlin, *Macromolecules* 1995, 28, 8713-8721.

"Stereoregular Precursors to Poly(*p*-phenylene) via Transition-Metal-Catalyzed Polymerization. 1. Precursor Design and Synthesis." D. L. Gin, V. P. Conticello, and R. H. Grubbs, *J. Am. Chem. Soc.* 1994, 116, 10507-10519.

"Stereoregular Precursors to Poly(*p*-phenylene) via Transition-Metal-Catalyzed Polymerization. 2. The Effects of Polymer Stereochemistry and Acid Catalysts on Precursor Aromatization." D. L. Gin, V. P. Conticello, and R. H. Grubbs, *J. Am. Chem. Soc.* 1994, 116, 10934-10947.

"Modeling Ring-Chain Equilibria in Ring-Opening Metathesis Polymerization (ROMP) of Cycloolefins." Z.-R. Chen, J. P. Claverie, R. H. Grubbs, J. A. Kornfield, *Macromolecules* 1995, 28, 2147-2154.

"New Syntheses of Benzobarrelenes." L. Pu and R. H. Grubbs, *J. Org. Chem.* 1994, 59, 1351-1353.